

# Constructing Ru particles decorated Co<sub>3</sub>B-CoP heterostructures as a highly active and reusable catalyst for H<sub>2</sub> generation by catalyzing NaBH<sub>4</sub> hydrolysis

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## ABSTRACT

Constructing an efficient and reusable catalyst for catalyzing NaBH<sub>4</sub> hydrolysis for H<sub>2</sub> production is of vital significance. Herein, the Ru particles decorated Co<sub>3</sub>B-CoP heterostructures are obtained by chemical reduction and gas-phase phosphating treatment. The strong electronic interaction and abundant heterojunctions between the Co<sub>3</sub>B-CoP substrate and Ru particles have been elucidated. The optimal Ru<sub>0.063</sub>/Co<sub>3</sub>B-CoP catalyst exhibits a fast hydrogen generation rate (8875.8 mL min<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>) and a high turnover frequency (636.0 min<sup>-1</sup>) at 25 °C, superior to most ever reported catalysts. The excellent NaBH<sub>4</sub> hydrolysis performance can be attributed to the lower activation energy (47.6 kJ mol<sup>-1</sup>) and the synergy between Co<sub>3</sub>B-CoP substrate and Ru particles. Density functional theory calculations show that electrons penetrate into Ru particles from Co<sub>3</sub>B-CoP substrate, in which the electron-rich Ru particles can selectively adsorb BH<sub>4</sub><sup>-</sup> ions, while the electron-deficient Co<sub>3</sub>B-CoP facilitates the capture of H<sub>2</sub>O molecules, thereby synergistically promote the catalyzing NaBH<sub>4</sub> hydrolysis to produce H<sub>2</sub>.

## 1. Introduction

With negative environmental issues and severe energy deficiency owing to the ongoing depletion of traditional fossil fuels, it is urging to seek clean and sustainable alternative energy [1]. Hydrogen (H<sub>2</sub>) has been deemed the most suitable energy carrier to replace fossil fuels due to its high energy density and environmental protection characteristics [2,3]. However, the production and storage of H<sub>2</sub> remain a great challenge for the widespread use and industrialization of hydrogen fuel cell devices [4]. Therefore, finding efficient, sustainable, and reusable hydrogen storage sources is imperative to realize safe production and storage of hydrogen [5].

Metal hydrides have received widespread attention owing to their advantage of high hydrogen storage capacity, non-toxicity and mild reaction conditions. Nowadays, the commonly used metal hydrogen storage materials include MgH<sub>2</sub> [6], LiAlH<sub>4</sub> [7], NaBH<sub>4</sub> [8], etc. Among them, NaBH<sub>4</sub> has a high hydrogen storage density (10.6 wt%), as well as stably stored in an alkaline solution, which is favorable to catalyze the hydrolysis of NaBH<sub>4</sub> to release H<sub>2</sub> in a controllable manner [9,10]. Most

notably, Zhu et al. successfully used a very simple, lightweight and effective ball milling technology to regenerate the by-products of NaBH<sub>4</sub>, realizing the reusability of NaBH<sub>4</sub> [11]. Benefiting from these feasible regeneration technologies, the application of H<sub>2</sub> generation by NaBH<sub>4</sub> hydrolysis has a broader industrialization prospect. Unfortunately, the self-hydrolysis of NaBH<sub>4</sub> suffers from sluggish kinetics, and is far from satisfying people's needs [12]. Driven by the requirements of rapid industrialization, it is necessary to add suitable catalysts to increase the rate of NaBH<sub>4</sub> hydrolysis to release hydrogen [13,14]. Generally, in order to inhibit the self-hydrolysis of NaBH<sub>4</sub>, NaOH is added as a stabilizer to achieve the purpose of producing hydrogen on demand. The ideal hydrolysis reaction equation of NaBH<sub>4</sub> is as follows [15]:



Many recent reports have proved that noble metal-based catalysts are remarkable catalysts for the hydrolysis of sodium borohydride, such as RuP<sub>3</sub>-CoP [16], Ru-Co/CNTs [17], Ru-Fe/GO [18], Rh/Co<sub>3</sub>O<sub>4</sub> [19], Pt/CeO<sub>2</sub> - Co<sub>7</sub>Ni<sub>2</sub>O<sub>x</sub> [20], etc. Nevertheless, the relatively high cost and

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scarcity of noble metals seriously affect their widespread industrial application. Suitable support can not only regulate the content of noble metals, but also enhance the catalytic activity through the synergistic effect of noble metals and support [21,22]. Recently, many cobalt-based catalysts have exhibited great potential activity for hydrogen production by  $\text{NaBH}_4$  hydrolysis [23,24].

Herein, we have successfully synthesized Ru clusters modified  $\text{Co}_3\text{B}$ - $\text{CoP}$  heterostructures through wet chemical reduction and gas-phase phosphating under  $\text{N}_2$ . Systematic characterization techniques have been applied to explore the crystallinity, microstructure, porosity, and chemical state of different components. Density functional theory (DFT) calculations show that the  $\text{Ru}_{0.063}/\text{Co}_3\text{B}-\text{CoP}$  catalyst has a lower chemical potential for hydrogen hydrolysis. Performance tests demonstrate that  $\text{Ru}_{0.063}/\text{Co}_3\text{B}-\text{CoP}$  catalyst exhibits high hydrogen generation rate (HGR,  $8875.8 \text{ mL H}_2 \text{ min}^{-1} \text{ g}_{\text{cat}}^{-1}$ ) and turnover frequency (TOF,  $636.0 \text{ mol min}^{-1} \text{ mol}_{\text{Ru}}^{-1}$ ) values, as well as a low activation energy ( $47.6 \text{ kJ mol}^{-1}$ ). This outstanding catalytic performance can be attributed to the strong electronic interaction between  $\text{Co}_3\text{B}-\text{CoP}$  substrate and Ru particles, which facilitates to the capture and cleavage of  $\text{H}_2\text{O}$  molecules and  $\text{BH}_4^-$  ions, respectively, thereby accelerating the catalytic hydrolysis of  $\text{NaBH}_4$  for  $\text{H}_2$  production.

## 2. Experimental section

### 2.1. Materials

Cobalt(II) chloride hexahydrate ( $\text{CoCl}_2 \cdot 6 \text{ H}_2\text{O}$ ), Sodium borohydride ( $\text{NaBH}_4$ ), Sodium hydroxide ( $\text{NaOH}$ ), Sodium hypophosphite ( $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ ), Cobalt(II) nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O}$ ), Hexamethylenetetramine ( $\text{C}_6\text{H}_{12}\text{N}_4$ ), and Ruthenium(III) chloride hydrate ( $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ ). All chemicals are analytically pure and can be used without further purification. The aqueous solutions in this work were prepared from ultrapure water with a resistivity of  $18.2 \text{ M}\Omega \cdot \text{cm}$ , obtained from a UPTA-20 water purification system (China Shanghai Lichen Bangxi Instrument Technology Co., Ltd.).

### 2.2. Synthesis of $\text{Co}_3\text{B}$

The synthetic process of  $\text{Co}_3\text{B}$  referred to the reported literature with some modifications [25]. Typically, 30.0 mL of  $\text{CoCl}_2$  solution (0.5 M) was placed in ice water bath and stirred magnetically. Subsequently, Ar was rinsed in the solution for 30 min, and then 10.0 mL of  $\text{NaBH}_4$  solution (1.0 M) was added dropwise to the solution, followed by stirring for another 30 min. After centrifugation and washing with water several times, as well as vacuum drying at  $60^\circ\text{C}$  for 12 h, a black  $\text{Co}_3\text{B}$  powder was obtained.

### 2.3. Synthesis of $\text{Co}_3\text{B}-\text{CoP}$

The  $\text{Co}_3\text{B}-\text{CoP}$  heterostructure was synthesized with  $\text{Co}_3\text{B}$  and  $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$  as precursors. Specifically, 1.0 g of  $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$  was on the upstream, and 0.08 g of  $\text{Co}_3\text{B}$  were placed in the downstream. The tube furnace was heated to  $350^\circ\text{C}$  ( $5^\circ\text{C min}^{-1}$ ) in  $\text{N}_2$  atmosphere and maintained for 2 h. After natural cooling, the received precursor was denoted as  $\text{Co}_3\text{B}-\text{CoP}$ .

### 2.4. Synthesis of $\text{Ru}/\text{Co}_3\text{B}-\text{CoP}$

In a typical procedure, 30.0 mg as-synthesized  $\text{Co}_3\text{B}-\text{CoP}$  were ultrasonically dispersed in 20.0 mL deionized water containing 9.0 mg (or 3.0, 6.0, 12.0 and 15.0 mg)  $\text{RuCl}_3$ , and allowed to react at room temperature for 4 h with stirring. Subsequently, 10.0 mL of 0.08 M  $\text{NaBH}_4$  solution was added dropwise to above mixture and reacted for another 30 min. The product was collected by centrifugation, washed several times with abundant  $\text{H}_2\text{O}$ , and then vacuum dried at  $60^\circ\text{C}$  for 12 h. Commercial  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  is used to prepare a specific concentration

solution and then disperse it with a certain amount of substrate weighed accurately. An excessive amount of reducing agent is used to ensure the complete reaction of Ru ions. The mass content of Ru determined by ICP-AES measurement was 6.3 wt%, so the product was labelled as  $\text{Ru}_{0.063}/\text{Co}_3\text{B}-\text{CoP}$ , where the subscript 0.063 represented the mass percentage of Ru. Repeated experiments ensure the reproducibility of the catalyst. For comparison,  $\text{Ru}_{0.02}/\text{Co}_3\text{B}-\text{CoP}$ ,  $\text{Ru}_{0.047}/\text{Co}_3\text{B}-\text{CoP}$ ,  $\text{Ru}_{0.089}/\text{Co}_3\text{B}-\text{CoP}$  and  $\text{Ru}_{0.113}/\text{Co}_3\text{B}-\text{CoP}$  were also prepared by the same approach as that of  $\text{Ru}_{0.063}/\text{Co}_3\text{B}-\text{CoP}$ .

### 2.5. Synthesis of $\text{Ru}/\text{CoP}$

Typically, 0.58 g  $\text{Co}(\text{NO}_3)_2$  and 0.56 g hexamethylenetetramine were dissolved in 15.0 mL deionized water with stirring for 30 min to obtain a uniform solution. Next, the mixture was transferred to a 50 mL Teflon-lined autoclave and raised to  $100^\circ\text{C}$  for 10 h. After natural cooling, the product was collected by centrifugation, washed and then freeze-dried overnight. As a comparison,  $\text{Co}(\text{OH})_2$  was first phosphated to  $\text{CoP}$  using vapor-phase phosphating, and then Ru precursor was deposited on  $\text{CoP}$  surface ( $\text{Ru}/\text{CoP}$ ) by chemical reduction as described above.

### 2.6. Catalytic measurements

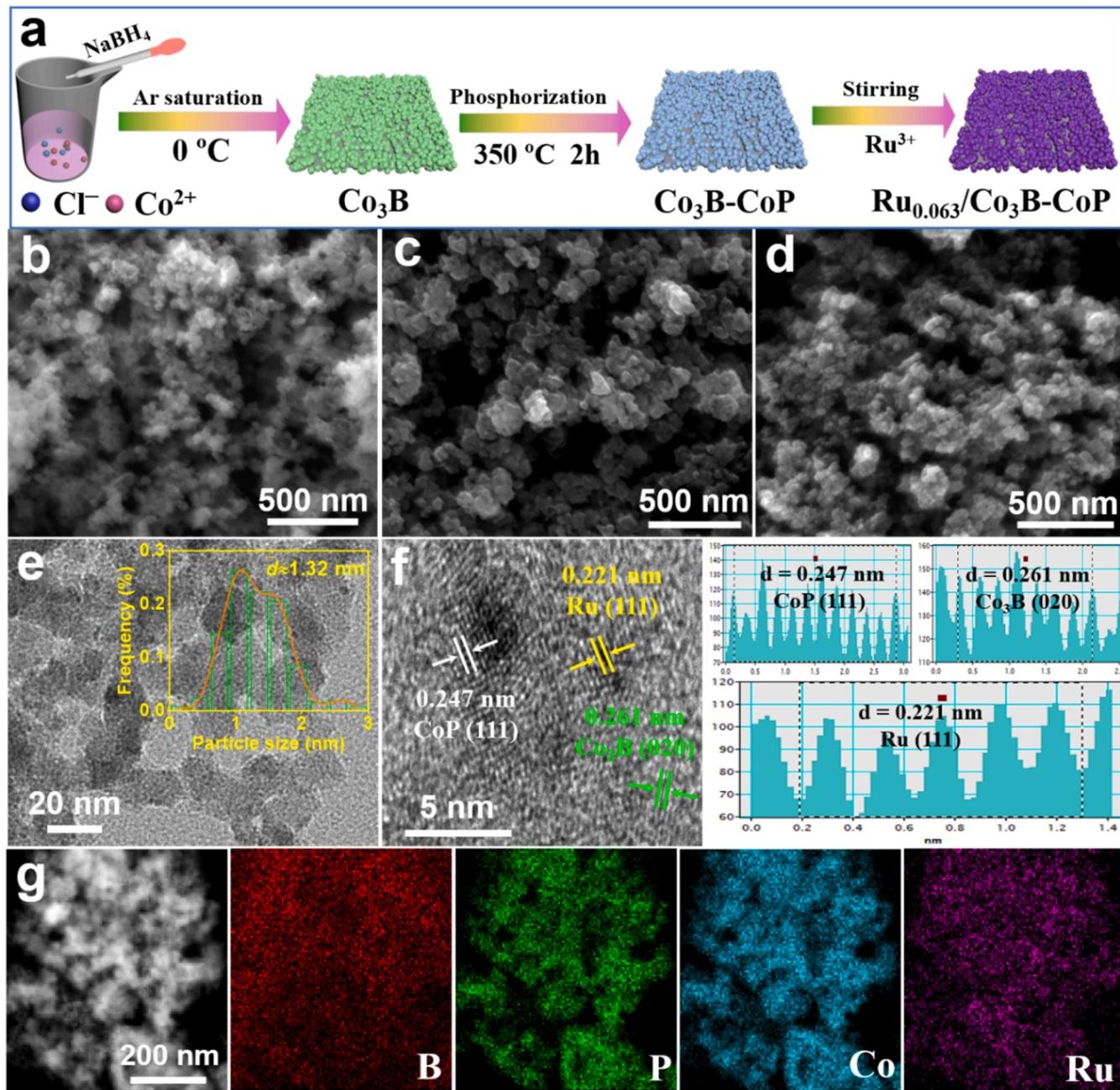
The hydrolysis rate, activation energy and reusability of  $\text{NaBH}_4$  were obtained to evaluate the performance of catalysts through following methods. Generally, 50 mL of 150 mM  $\text{NaBH}_4 + 0.4 \text{ wt\% NaOH}$  solution was injected into a 100 mL three-necked round-bottom flask, which was then placed in a water bath at 298 K and stirred for 30 min until the temperature remained constant. Subsequently, 10.0 mg of the catalyst was added to the above solution and stirred magnetically. The generated  $\text{H}_2$  was collected by the drainage approach, which connected to a computer to record the change of water quality instantly. For recyclability testing of catalysts, we continued to replace the completely decomposed  $\text{NaBH}_4$  solution with fresh one for five consecutive cycles at 298 K. After each stability test, the catalytic material was centrifuged, washed and vacuum dried, as well as weighed the catalytic material. All experiments were repeated three times to ensure reliable results. For the evaluation of the activation energy of catalysts, the reaction temperature was controlled from 298 K to 318 K for the catalytic hydrolysis of  $\text{NaBH}_4$ , and then the activation energy was calculated by the Arrhenius formula.

## 3. Results and discussion

### 3.1. Synthesis strategy and microstructure analysis

The  $\text{Ru}/\text{Co}_3\text{B}-\text{CoP}$  catalyst is constructed by the following multistep fabrication procedures (Fig. 1a). Firstly, the magnetic  $\text{Co}_3\text{B}$  is synthesized in an ice bath under Ar protection. Among them, the strong reducing agent  $\text{NaBH}_4$  makes the preparation process of  $\text{Co}_3\text{B}$  extremely rapid and violent, while the low temperature environment can weaken the reaction and reduce the aggregation of  $\text{Co}_3\text{B}$  particles (Fig. 1b). Subsequently, using  $\text{NaH}_2\text{PO}_2$  as the phosphorus source,  $\text{Co}_3\text{B}$  is phosphatized to  $\text{Co}_3\text{B}-\text{CoP}$  heterostructure under  $\text{N}_2$  atmosphere. Fig. 1c presents that  $\text{Co}_3\text{B}-\text{CoP}$  retains its initial shape with slightly larger size and smoother surface, which caused by the 2 h aging process at  $350^\circ\text{C}$ . Since the reduction potential of  $\text{NaBH}_4$  (1.24 V) is much higher than that of  $\text{Ru}^{3+}/\text{Ru}$  (0.75 V), Ru ions are reduced to form the target catalyst when the two precursors are initially contacted; thereby, the Ru precursor is successfully reduced and anchored on the surface of the  $\text{Co}_3\text{B}-\text{CoP}$  composite before behaving as the hydrolysis catalyst. The as-prepared  $\text{Ru}_{0.063}/\text{Co}_3\text{B}-\text{CoP}$  hybrid composite still maintains a particulate structure with almost no visible changes (Fig. 1d).

Transmission electron microscopy (TEM) is further performed to analyze the microstructure of  $\text{Ru}_{0.063}/\text{Co}_3\text{B}-\text{CoP}$ . The  $\text{Co}_3\text{B}$ ,  $\text{Co}_3\text{B}-\text{CoP}$ ,

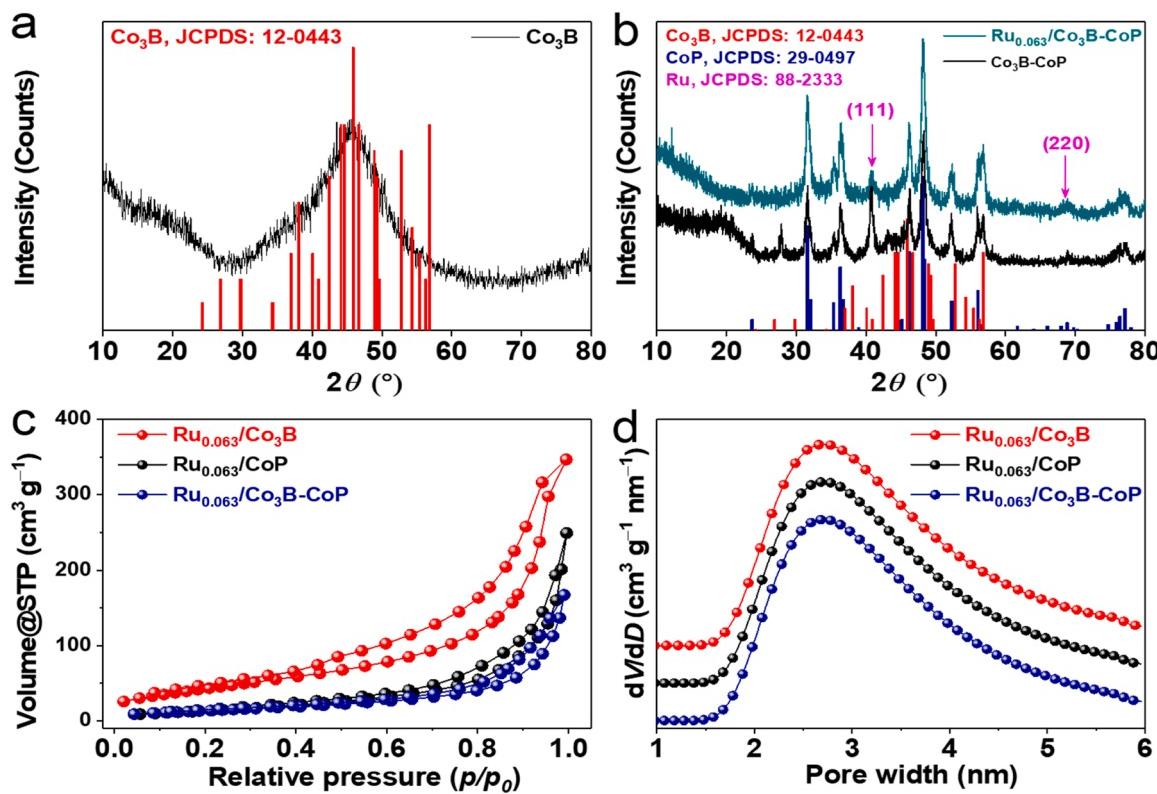


**Fig. 1.** (a) Schematic diagram of Ru<sub>0.063</sub>/Co<sub>3</sub>B-CoP synthesis. SEM images of (b) Co<sub>3</sub>B, (c) Co<sub>3</sub>B-CoP, and (d) Ru<sub>0.063</sub>/Co<sub>3</sub>B-CoP. (e) TEM image with inset particle size distribution of Ru particles, and (f) HRTEM image of Ru<sub>0.063</sub>/Co<sub>3</sub>B-CoP. (g) HAADF-STEM image and elemental mappings of Ru<sub>0.063</sub>/Co<sub>3</sub>B-CoP (B, P, Co and Ru).

and Ru<sub>0.063</sub>/Co<sub>3</sub>B-CoP catalysts are nanoparticles with a 50–200 nm grain size (Fig. 1b, c, and d). As shown in Fig. 1e, the Ru particles are dispersed uniformly throughout the catalyst, with an average cluster size of 1.32 nm. While the average sizes of Ru particles for Ru<sub>0.063</sub>/CoP and Ru<sub>0.063</sub>/Co<sub>3</sub>B catalysts are 1.84 and 1.95 nm, respectively (Fig. S1), indicating that the Co<sub>3</sub>B-CoP heterostructure has a positive effect on the dispersion of Ru particles [26]. Meanwhile, the high-resolution TEM images revealed that the Ru on the surface is composed of Ru (111, 0.221 nm) [27]. Moreover, the crystal orientation and the lattice spacing of Co<sub>3</sub>B (020, 0.261 nm) and CoP (111, 0.247 nm) are also detected (Fig. 1f) [28,29]. In addition, the high-annular dark-field scanning TEM (HAADF-STEM) image and corresponding element mappings (Fig. 1g) demonstrate the uniform distribution of B, P, Co, and Ru throughout the composite [30].

### 3.2. Crystal structure analysis

The phase composition and crystal structure of the composite was elucidated by X-ray diffraction (XRD). As displayed in Fig. 2a, the diffraction peaks, which concentrated between 30 and 60 ° are indexed to the standard diffraction peaks (JCPDS: 12–0443) of orthorhombic Co<sub>3</sub>B [31]. After the phosphating treatment, in addition to the diffraction peaks of Co<sub>3</sub>B, signals of typical orthorhombic CoP (JCPDS: 29–0497) can be detected at the same time [32], confirming the successful formation of the Co<sub>3</sub>B-CoP composite (Fig. 2b). After the reduction of Ru species on the Co<sub>3</sub>B-CoP surface, new peaks appeared at 40.7 °, and 69.7 ° were attributed to the (111) and (220) crystal planes of Ru (JCPDS: 88–2333), indicating that Ru was successfully formed [33]. Furthermore, Figs. S2a-b showed that the as-prepared Co(OH)<sub>2</sub> and CoP are consistent with the corresponding standard spectra, and Ru signals

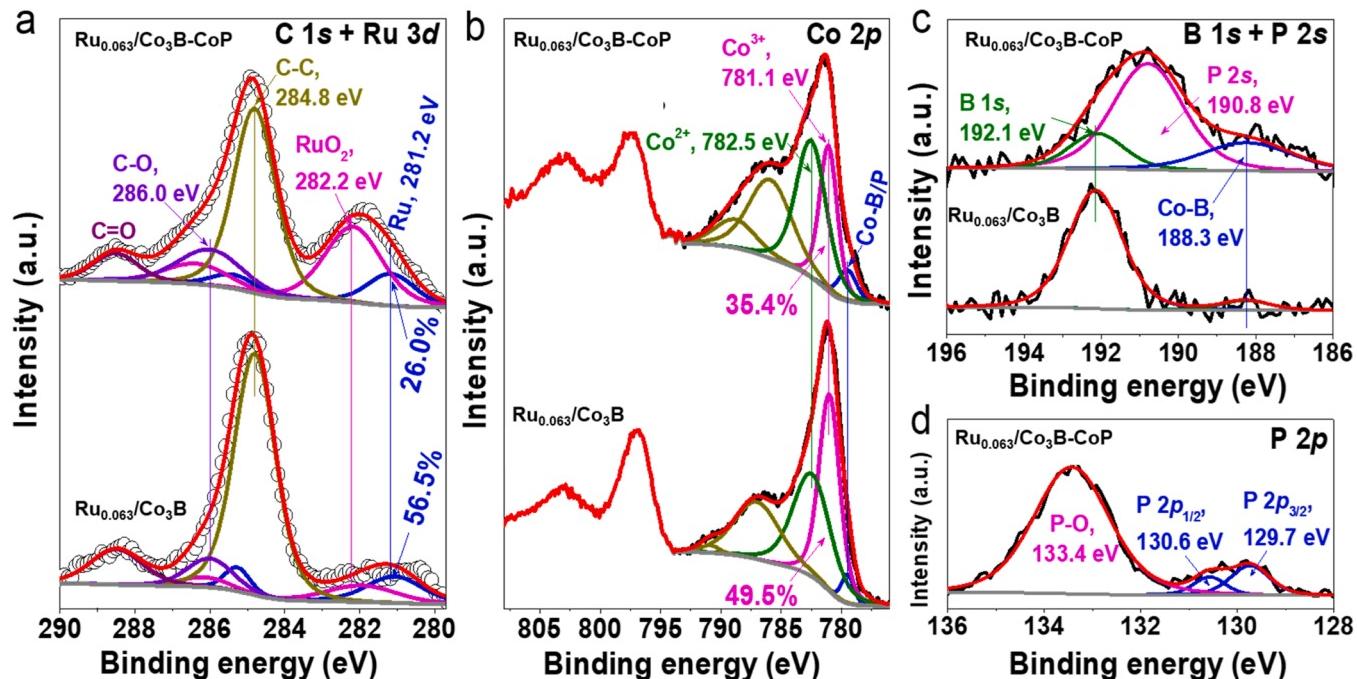


**Fig. 2.** XRD patterns of (a)  $\text{Co}_3\text{B}$ , (b)  $\text{Co}_3\text{B}-\text{CoP}$  and  $\text{Ru}_{0.063}/\text{Co}_3\text{B}-\text{CoP}$ . (c)  $\text{N}_2$  adsorption–desorption isotherms and (d) the corresponding pore size distribution curves of  $\text{Ru}_{0.063}/\text{Co}_3\text{B}$ ,  $\text{Ru}_{0.063}/\text{CoP}$  and  $\text{Ru}_{0.063}/\text{Co}_3\text{B}-\text{CoP}$ .

were also detected in  $\text{Ru}_{0.063}/\text{CoP}$  composite (Fig. S2c).

As presents in Fig. 2c, the textural features of the samples are investigated by  $\text{N}_2$  adsorption–desorption isotherm. It exhibits a type III isotherm with typical hysteresis loop, indicating that the materials have the characteristics of mesoporous structure [34]. The Brunauer–Emmett–Teller (BET) surface areas of the  $\text{Ru}_{0.063}/\text{Co}_3\text{B}$ ,

$\text{Ru}_{0.063}/\text{CoP}$  and  $\text{Ru}_{0.063}/\text{Co}_3\text{B}-\text{CoP}$  are  $161.0$ ,  $54.8$  and  $50.4 \text{ m}^2 \text{ g}^{-1}$ , respectively. Notably, the corresponding pore size distribution curves of all catalysts are similar, and the pore size is about  $2.6 \text{ nm}$  (Fig. 2d), which is mainly caused by the cracks and porous structures in the composite [35]. Besides, the specific surface areas of  $\text{Co}_3\text{B}$ ,  $\text{CoP}$  and  $\text{Co}_3\text{B}-\text{CoP}$  are  $49.0$ ,  $7.1$  and  $9.9 \text{ m}^2 \text{ g}^{-1}$ , respectively (Fig. S3), indicating



**Fig. 3.** High-resolution XPS spectra of (a)  $\text{C } 1\text{s} + \text{Ru } 3\text{d}$ , (b)  $\text{Co } 2\text{p}$ , (c)  $\text{B } 1\text{s} + \text{P } 2\text{s}$ , (d)  $\text{P } 2\text{p}$  regions of  $\text{Ru}_{0.063}/\text{Co}_3\text{B}$  and/or  $\text{Ru}_{0.063}/\text{Co}_3\text{B}-\text{CoP}$ .

CoP blocked some of the surface areas of the Co<sub>3</sub>B. Similar findings are reported in the literature [36,37]. The higher surface area exposes more active sites; meanwhile, the high porosity helps the gas to diffuse along the surface. Moreover, nano-level dispersion of the conductive Ru particles enhances surface conductivity, which is suggested by lower resistance. The synergistic interaction between different components plays a more critical role in improving catalytic activity.

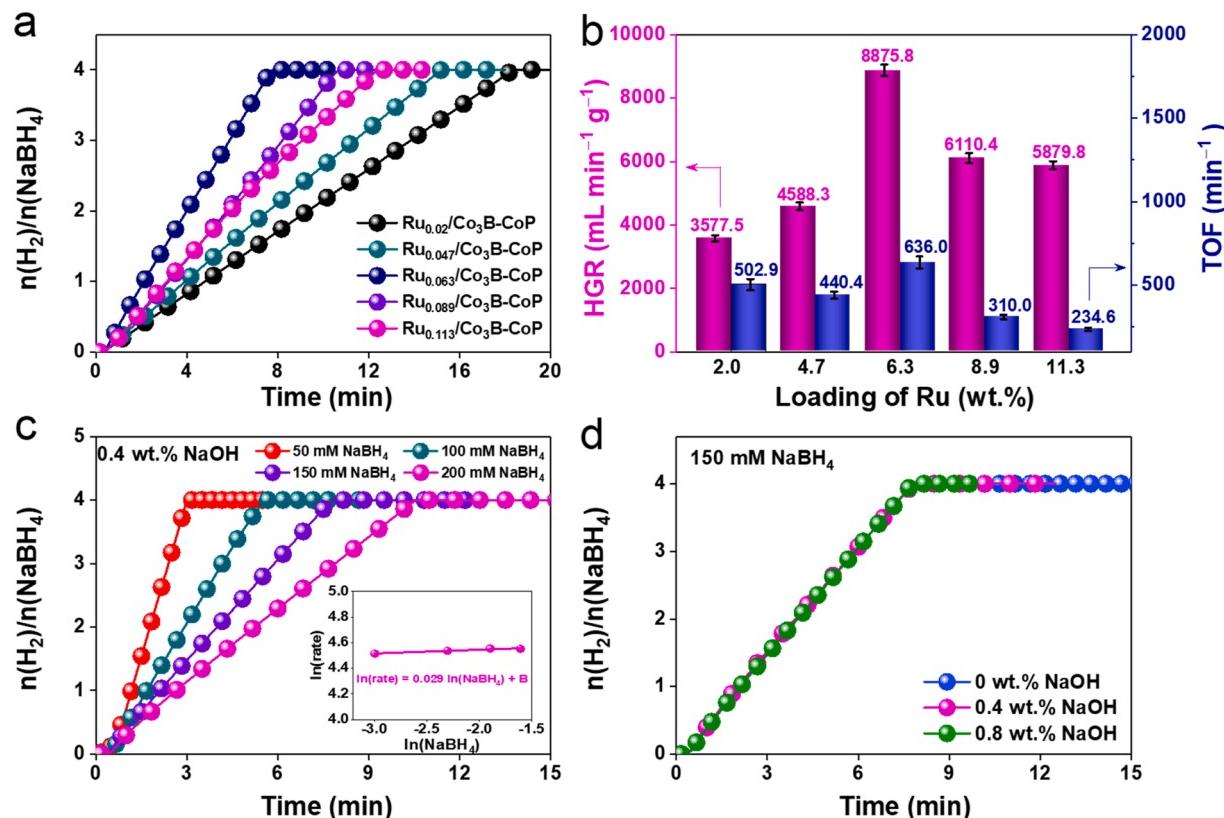
### 3.3. XPS analysis

The elemental composition and chemical state of the catalyst are further elucidated by X-ray photoelectron spectroscopy (XPS). XPS analysis of the catalysts confirm coexistence of C, O, B, P, Co and Ru elements (Fig. S4). The high-resolution XPS spectra of C 1s + Ru 3d regions are convoluted into two strong peaks at C–C (284.8 eV) and C–O (286.0 eV) and regarded as calibration standard [38], while the binding energies at 281.2 and 282.2 eV are in turn corresponding to 3d<sub>5/2</sub> of Ru metal and RuO<sub>2</sub> (Fig. 3a) [39,40]. The XPS results demonstrate chemical reduction of metallic Ru with 26.0% atomic percentage on the surface of Co<sub>3</sub>B-CoP, which are much lower than that of Co<sub>3</sub>B (56.5%), indicating that the surface characteristics of the composite can effectively adjust the chemical state of attachments. The oxidation reaction is unavoidable upon exposure to the air since the particle size of the Ru is very small and has a high surface area, which makes it easily oxidized. A similar observation on Ru-WO<sub>3</sub> and RuNi/CQDs was reported in the literature [41,42]. Since the oxidation of the Ru catalyst occurs only on the surface and the RuO<sub>2</sub> is reduced back to Ru during the NaBH<sub>4</sub> hydrolysis, the oxidation does not affect the performance. To be consistent with the literature reports [43,44], the Ru<sub>0.063</sub>/Co<sub>3</sub>B-CoP was used. Similar examples of reduced metallic Ru content and increased RuO<sub>2</sub> content were also observed for P-vacancy-rich CoP surfaces in our previous study [45].

As shown in Fig. 3b, the high-resolution Co 2p XPS spectra of Ru<sub>0.063</sub>/Co<sub>3</sub>B-CoP and Ru<sub>0.063</sub>/Co<sub>3</sub>B are deconvoluted into Co-B/P (779.5 eV), Co<sup>3+</sup> (781.1 eV), Co<sup>2+</sup> (782.5 eV) and two satellite peaks, respectively [16]. The results indicate that the Co<sup>3+</sup> content in Ru<sub>0.063</sub>/Co<sub>3</sub>B-CoP is 35.4%, which is much lower than that in Ru<sub>0.063</sub>/Co<sub>3</sub>B (49.5%). This significant change in the chemical states of Ru and Co oxide species reflects the strong electronic interaction between them, which is speculated to be a key factor in improving the catalytic hydrolysis performance. Additionally, the high-resolution B 1s + P 2s further confirms the formation of Co-B alloy (B 1s of Co-B at 188.3 eV) in the two materials (Fig. 3c) [25,46]. The high-resolution P 2p indicates that there are abundant CoP components (P 2p of Co-P at 129.7 eV for 2p<sub>3/2</sub> and 130.6 eV for 2p<sub>1/2</sub>) in the Ru<sub>0.063</sub>/Co<sub>3</sub>B-CoP composite (Fig. 3d) [47].

### 3.4. Catalytic hydrolysis analysis

The performance test of the catalyst is usually carried out in the solution of 150 mM NaBH<sub>4</sub> (containing 0.4 wt% NaOH) at 25 °C, and the schematic diagram of reaction device is shown in Fig. S5. In previous studies, we have found that the weak self-decomposition reaction occurs in the NaBH<sub>4</sub> aqueous solution (Fig. S6), and the extremely small HGR cannot meet people's needs. Considering that NaBH<sub>4</sub> can exist stably in alkaline solution (Fig. S7), we can produce H<sub>2</sub> on demand using catalysts. Here, a series of Ru-modified Co<sub>3</sub>B-CoP catalysts were used to investigate the effect on the hydrolysis of NaBH<sub>4</sub>. The mass percentage content of Ru particles in different catalysts is determined by ICP-AES (Table S2), which are 2.0, 4.7, 6.3, 8.9 and 11.3 wt%, respectively. As shown in Fig. 4a, the HGR presents a parabolic form with the increase of Ru species content, and when the loading is 6.3 wt%, it has the highest HGR value. Fig. 4b reveals that the optimal Ru<sub>0.063</sub>/Co<sub>3</sub>B-CoP catalyst possesses a HGR value reaching up to 8875.8 mL min<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>, and the TOF is 636.0 mol min<sup>-1</sup> mol<sub>Ru</sub><sup>-1</sup>, outperforming most documented



**Fig. 4.** Effect of catalytic NaBH<sub>4</sub> hydrolysis for H<sub>2</sub> generation under different conditions. (a) Different amounts of Ru. (b) The summarized TOF and HGR values. (c) The influence of NaBH<sub>4</sub> content on HGR at 0.4 wt% NaOH concentration (Inset: the corresponding plot of ln (rate) vs ln (concentration of NaBH<sub>4</sub>)). (d) The influence of NaOH content on HGR with NaBH<sub>4</sub> concentration for 150 mM. All tests are performed at 298 K.

catalysts (Table S3). The high-efficiency catalytic performance can be attributed to the strong interaction between the different components in the Ru<sub>0.063</sub>/Co<sub>3</sub>B-CoP catalyst, and the suitable Ru content can form more grain boundaries, thereby exposing more active sites [48,49].

In order to explore the effect of NaBH<sub>4</sub> concentration on catalytic H<sub>2</sub> production, we kept NaOH concentration constant under different NaBH<sub>4</sub> concentrations. As shown in Fig. 4c, the HGR value remained almost constant with increasing NaBH<sub>4</sub> concentration in the 50–200 mM range. The relationship between ln (rate) and ln (concentration of NaBH<sub>4</sub>) is fitted in the inset of Fig. 4c, and the slope value obtained corresponds to 0.029, which is close to zero. The results suggested that the hydrolysis reaction of NaBH<sub>4</sub> was a zero-level reaction, independent of the concentration of NaBH<sub>4</sub> [50]. Meanwhile, the effect of alkalinity on catalytic hydrolysis performance of NaBH<sub>4</sub> is also explored. In Fig. 4d, when the NaBH<sub>4</sub> concentration is fixed at 150 mM, the corresponding HGR is almost unaffected as the NaOH content changes. The effect of NaOH concentration on the HGR of Ru<sub>0.063</sub>/Co<sub>3</sub>B-CoP catalyst is consistent with the report by Wei et al. [51]. However, Yao et al. reported that the HGR of NaBH<sub>4</sub> hydrolysis was positively correlated with NaOH concentration in a specific concentration range; nevertheless, the HGR would decrease with a further increase in NaOH concentration [52]. These results suggest that the influence of NaOH concentration on NaBH<sub>4</sub> hydrolysis largely depends on the composition of the catalyst [53]. The kinetic studies revealed that the NaBH<sub>4</sub> hydrolysis follows “zero” order kinetics, and OH<sup>-</sup> is one of the reactants [54]. Therefore, in theory, NaOH concentration should not affect the H<sub>2</sub> generation rate. Based on the above results, 150 mM NaBH<sub>4</sub> concentration and 0.4 wt% NaOH are selected as the solution for the study.

The factors affecting the hydrolysis of NaBH<sub>4</sub> for H<sub>2</sub> production are further analyzed using a series of comparative samples. As shown in Fig. 5a-b, Co<sub>3</sub>B, CoP and Co<sub>3</sub>B-CoP catalysts have lower HGR values for catalyzing NaBH<sub>4</sub> hydrolysis. Surprisingly, after loading the same amount of Ru on the above-mentioned substrates, the catalytic performances of Co<sub>3</sub>B, CoP and Co<sub>3</sub>B-CoP were enhanced by 2.01, 2.87 and 8.47 times, respectively, among which the Ru<sub>0.063</sub>/Co<sub>3</sub>B-CoP catalyst exhibits a maximum HGR value of 8875.8 mL H<sub>2</sub> min<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>. Fig. 5b shows that the HGR values of Co<sub>3</sub>B and CoP are very close, even though

the surface areas are different. This suggests the specific surface area is not a significant factor in determining the performance in this particular case. Moreover, combined with the poor performance of a single Ru catalyst (3012.2 mL H<sub>2</sub> min<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>, Fig. S8), the excellent catalytic NaBH<sub>4</sub> hydrolysis performance of Ru<sub>0.063</sub>/Co<sub>3</sub>B-CoP is attributed to the synergy between the Co<sub>3</sub>B-CoP and Ru particles [55]. In this study, the novelty can be summarized as a scalable process, low-cost noble metal-based catalyst, and outstanding efficiency [56–58]. To analyze the activation energy of the catalyst, HGR is tested at different temperatures from 298 to 318 K. As shown in Fig. S9 and Fig. 5c, the HGR of Co<sub>3</sub>B-CoP and Ru<sub>0.063</sub>/Co<sub>3</sub>B-CoP catalysts enhance rapidly with increasing temperature. The activation energy of the Ru<sub>0.063</sub>/Co<sub>3</sub>B-CoP catalyst is 47.6 kJ mol<sup>-1</sup>, which is lower than that of the Co<sub>3</sub>B-CoP catalyst (Fig. 5d) and many previously reported catalysts but not the lowest (Table S3). The low activation energy implies that the Ru<sub>0.063</sub>/Co<sub>3</sub>B-CoP catalyst has a lower energy barrier, thereby has a faster reaction kinetics during the reaction process [59].

Reusability is a crucial indicator for evaluating the performance of a catalyst, which is assessed through a continuous circulation test in 150 mM NaBH<sub>4</sub> (containing 0.4 wt% NaOH) solution. After each cycle of testing, we collect and vacuum dry the samples by centrifugation, and then add fresh NaBH<sub>4</sub> solution to continue the test. Fig. 5e-f exhibit the HGR and TOF values of Ru<sub>0.063</sub>/Co<sub>3</sub>B-CoP catalyst after five cycles, where the TOF value decreases from 645.5 to 443.9 min<sup>-1</sup>. Owing to the catalyst loss during catalyst recovery and Ru leaching, the catalytic rate reduces to 68.8% of the original. The morphology (Fig. S10) and crystal structure (Fig. S11) of the Ru<sub>0.063</sub>/Co<sub>3</sub>B-CoP are slightly changed. Meanwhile, the TEM image of the Ru<sub>0.063</sub>/Co<sub>3</sub>B-CoP catalyst after five cycles of stability tests shows that the average particle size of Ru nanoparticles is 1.68 nm (Fig. S12). The high-resolution XPS spectra of Ru 3d and Co 2p prove that the chemical states of the elements have changed significantly; for example, the content of Ru metal and Co<sup>3+</sup> increase markedly after five cycles (Fig. S13). The increase in the Ru metal content could be due to the robust reduction environment, and the growing Co<sup>3+</sup> content could indicate the Co<sub>3</sub>B leaching. The analysis suggests that the change of surface chemical states mainly cause the continuous decrease in catalytic performance, the exfoliation of Ru

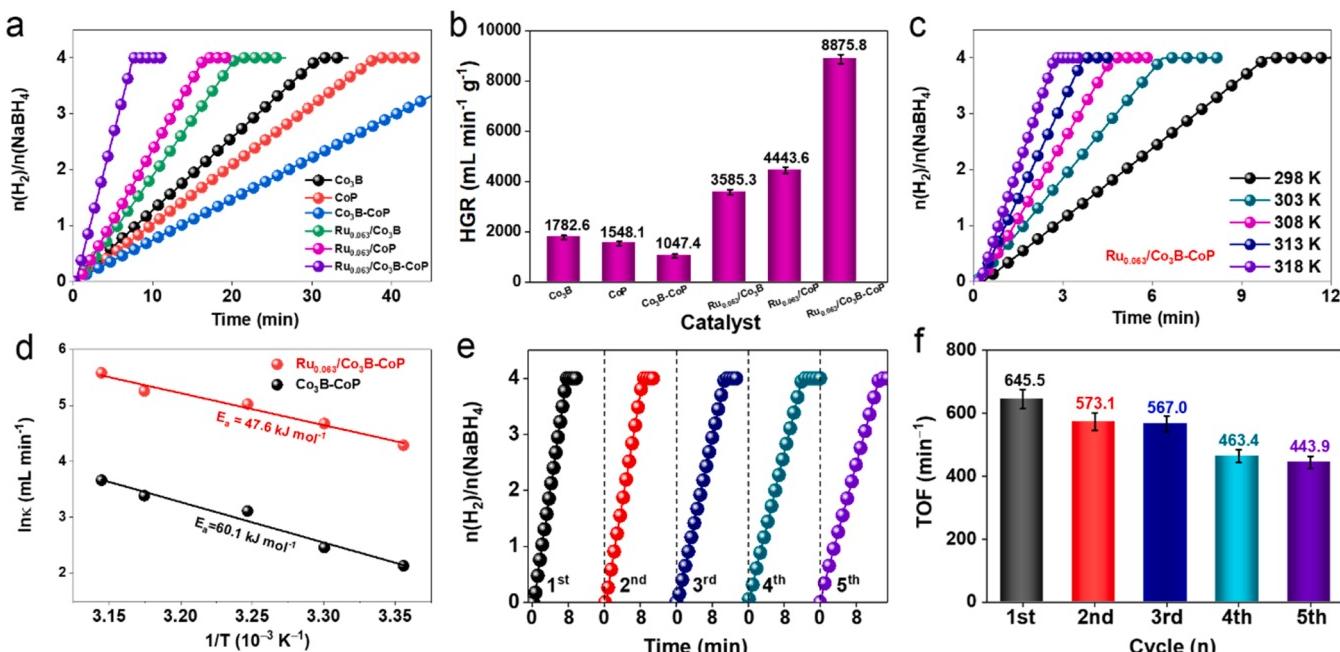


Fig. 5. (a) The relationship between the H<sub>2</sub> generation rates and reaction time of different catalysts, and (b) the summarized HGR values. (c) The relationship between catalytic NaBH<sub>4</sub> hydrolysis temperature and HGR in the range of 298–318 K. (d) The summarized Arrhenius diagram of Ru<sub>0.063</sub>/Co<sub>3</sub>B-CoP and Co<sub>3</sub>B-CoP. (e) Cycle stability test of Ru<sub>0.063</sub>/Co<sub>3</sub>B-CoP catalyst. (f) The summarized TOF values from e. All tests are performed in 150 mM NaBH<sub>4</sub> + 0.4 wt% NaOH solution.

particles (Table S2) and  $\text{BO}_2^-$  poisoning [60].

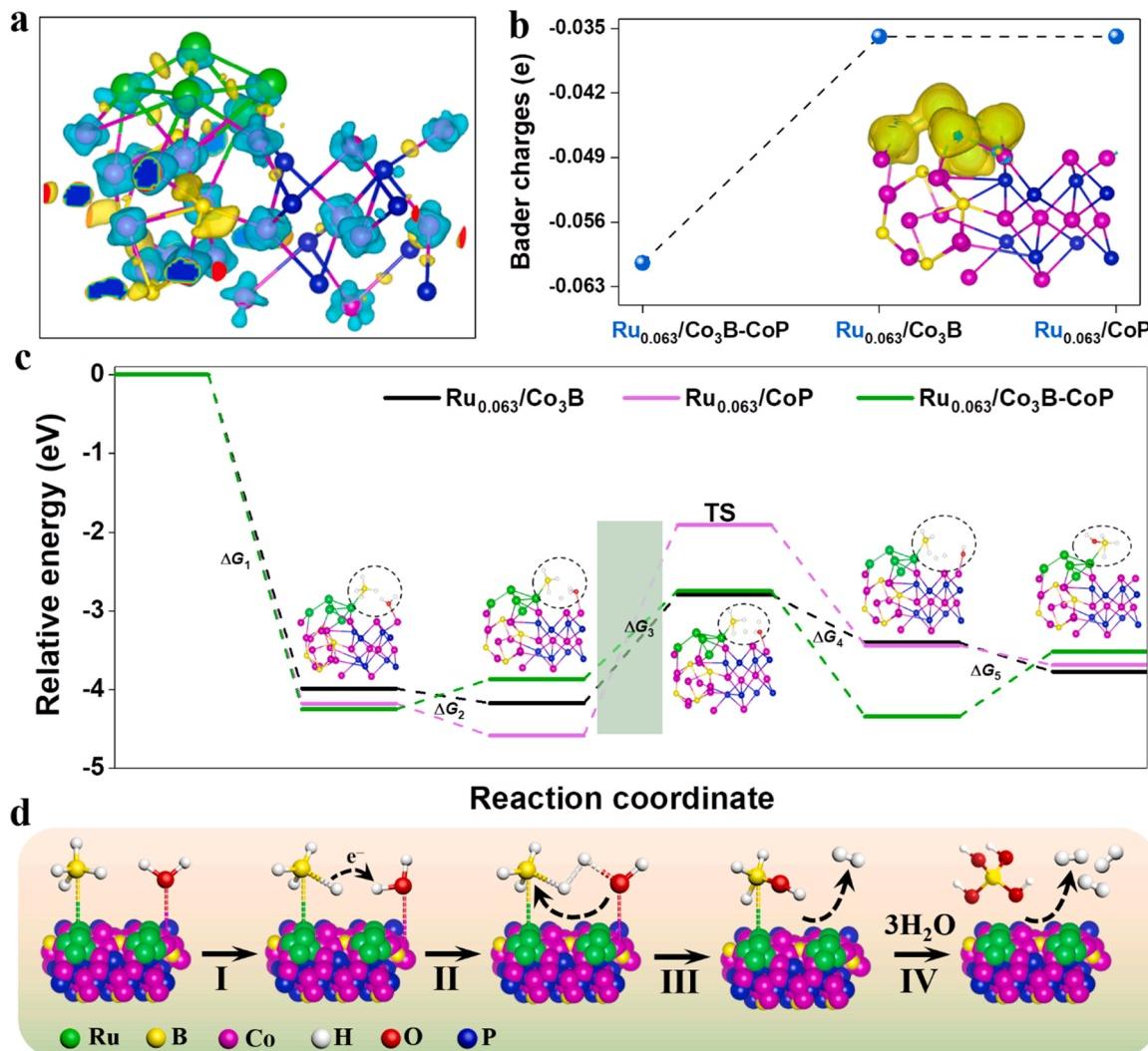
### 3.5. DFT calculations

DFT calculation is conducted to understand the superior catalytic hydrolysis performance. Systematic studies have demonstrated that half of the hydrogens produced by the  $\text{NaBH}_4$  hydrolysis come from water, which is favourable to improving hydrogen yield (Eq. 1) [61]. As shown in Fig. 6a, the deformed charge density distribution of the heterostructure presents a significant charge accumulation at the interface of two materials, confirming the strong synergistic effect between Ru and  $\text{Co}_3\text{B}-\text{CoP}$ . Subsequently, we investigate the Bader charges of Ru atoms on  $\text{Ru}_{0.063}/\text{CoP}$ ,  $\text{Ru}_{0.063}/\text{Co}_3\text{B}$  and  $\text{Ru}_{0.063}/\text{Co}_3\text{B}-\text{CoP}$  catalysts, and the charges adsorbed on Ru are  $-0.0045\text{ e}$ ,  $-0.035\text{ e}$  and  $-0.0604\text{ e}$  (Fig. 6b), respectively. Meanwhile, the charge distribution of the adsorbed  $\text{BH}_4^-$  ions indicates that the B ions are positively charged (Fig. S14). The results indicate that the electrons around Ru are enriched; thereby,  $\text{BH}_4^-$  groups are more inclined to adsorb on the Ru site due to the partially positively charged B atom. Fig. S15 displays the schematic diagram of hydrogen production of  $\text{Ru}_{0.063}/\text{CoP}$ ,  $\text{Ru}_{0.063}/\text{Co}_3\text{B}$  and  $\text{Ru}_{0.063}/\text{Co}_3\text{B}-\text{CoP}$  catalysts. The adsorption energies of  $\text{BH}_4^* + \text{H}_2\text{O}^*$  on the surfaces of  $\text{Ru}_{0.063}/\text{CoP}$ ,  $\text{Ru}_{0.063}/\text{Co}_3\text{B}$  and  $\text{Ru}_{0.063}/\text{Co}_3\text{B}-\text{CoP}$  catalysts are  $-4.17$ ,  $-3.98$  and

$-4.24\text{ eV}$ , respectively, indicating that  $\text{BH}_4^* + \text{H}_2\text{O}^*$  species are adsorbed readily to the surface of Ru particles in  $\text{Ru}_{0.063}/\text{Co}_3\text{B}-\text{CoP}$  (Fig. 6c). Meanwhile, comparing with  $\text{Ru}_{0.063}/\text{CoP}$  ( $\Delta G_3 = 1.38\text{ eV}$ ) and  $\text{Ru}_{0.063}/\text{Co}_3\text{B}$  ( $\Delta G_3 = 2.67\text{ eV}$ ), the optimized  $\text{Ru}_{0.063}/\text{Co}_3\text{B}-\text{CoP}$  ( $\Delta G_3 = 1.12\text{ eV}$ ) exhibits the lowest energy barrier, implying the highest hydrogen production activity (Table S1).

### 3.6. Catalytic mechanism analysis

As discussed above, the designed  $\text{Ru}_{0.063}/\text{Co}_3\text{B}-\text{CoP}$  catalyst exhibits good catalytic activity, which is mainly related to the composition of hybrid materials and the strong interaction between different components. As shown in Fig. 6d, a possible reaction mechanism based on Langmuir-Hinshelwood model has been proposed to catalyze the hydrolysis of  $\text{NaBH}_4$  for  $\text{H}_2$  generation [62]. Initially, the dissolved  $\text{BH}_4^-$  ions are selectively adsorbed on the surface of the Ru particles due to the abundant vacant  $4d$  orbitals on Ru atoms [63]. This result is consistent with the transfer of electrons from  $\text{CoP}$  to Ru species caused by the work function (Ru:  $4.71\text{ eV}$ ,  $\text{RuO}_2$ :  $5.0\text{ eV}$ ,  $\text{CoP}$ :  $4.227\text{ eV}$  and CoB alloy) [45, 64], making the electron-rich Ru site to adsorb B atoms with a little positive charge in  $\text{BH}_4^-$  ions. DFT calculations further demonstrate that the  $\text{Co}_3\text{B}-\text{CoP}$  composite can donate more electrons to Ru particles



**Fig. 6.** (a) Schematic diagram of the deformed charge density distribution of catalyst  $\text{Ru}_{0.063}/\text{Co}_3\text{B}-\text{CoP}$  catalyst. The blue, pink, yellow, and green balls represent P, Co, B, and Ru atoms, respectively. (b) Bader charges of Ru atoms on  $\text{Ru}_{0.063}/\text{CoP}$ ,  $\text{Ru}_{0.063}/\text{Co}_3\text{B}$  and  $\text{Ru}_{0.063}/\text{Co}_3\text{B}-\text{CoP}$  catalysts. (c) The free energy curves of  $\text{Ru}_{0.063}/\text{CoP}$ ,  $\text{Ru}_{0.063}/\text{Co}_3\text{B}$  and  $\text{Ru}_{0.063}/\text{Co}_3\text{B}-\text{CoP}$  for the hydrolysis of sodium borohydride. (d) Catalytic mechanism diagram of  $\text{H}_2$  production by hydrolysis of  $\text{NaBH}_4$  based on Langmuir-Hinshelwood model.

compared with single CoP and Co<sub>3</sub>B, and the electron-rich Ru particles are beneficial for BH<sub>4</sub><sup>-</sup> adsorption and H<sub>2</sub> desorption during the catalytic hydrolysis process. Meanwhile, the electron-deficient binary Co<sub>3</sub>B-CoP sites can adsorb abundant water molecules. At the interface, the adsorbed H<sub>2</sub>O molecules can attack BH<sub>4</sub><sup>-</sup> ions to release a H<sub>2</sub> molecule and form a BH<sub>3</sub>OH<sup>-</sup> intermediate [65]. As the reaction proceeds, the remaining H atoms in the borohydride are replaced by OH<sup>-</sup> ions, which are eventually decomposed into B(OH)<sub>4</sub><sup>-</sup> species [66].

#### 4. Conclusions

In summary, the Ru<sub>0.063</sub>/Co<sub>3</sub>B-CoP heterostructure is successfully fabricated by chemical deposition and vapor phase phosphating process. Various characterization techniques, such as XRD, SEM, TEM, BET and XPS, have explored the crystal structure, morphology, porosity and chemical state of the material. The resulted Ru<sub>0.063</sub>/Co<sub>3</sub>B-CoP catalyst shows excellent catalytic activity in catalyzing the hydrolysis of NaBH<sub>4</sub> for H<sub>2</sub> generation. Based on various characterizations and reaction processes, a reliable catalytic mechanism is proposed. The analysis suggests that the change of the surface chemical state caused by the strong interaction between the components in the Ru<sub>0.063</sub>/Co<sub>3</sub>B-CoP catalyst is the key to improving the H<sub>2</sub> generation during the catalytic NaBH<sub>4</sub> hydrolysis process. This work has important theoretical and practical significance for the development of novel and efficient catalysts for H<sub>2</sub> production from NaBH<sub>4</sub> hydrolysis.

#### CRediT authorship contribution statement

**Shuqing Zhou:** Writing – original draft, Methodology. **Lianrui Cheng:** Data curation. **Yi Huang:** Investigation. **Yi Liu:** Methodology. **Luyan Shi :** Data curation, Investigation. **Tayirjan Taylor Isimjan:** Writing – review & editing. **Xiulin Yang:** Writing – review & editing, Supervision.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data Availability

The data that has been used is confidential.

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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2023.122519](https://doi.org/10.1016/j.apcatb.2023.122519).

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